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(54) Title: CASTING STEEL STRIP

(57) **Abstract:** Twin roll casting of thin steel strip. Molten steel is introduced between a pair of cooled casting rolls to form a casting pool from which steel solidifies on the rolls to produce a solidified strip. The molten steel has a total oxygen content in the range 100ppm to 250ppm and contains metal oxide inclusions comprising any one or more of MnO, $SiO_2$ and $Al_2O_3$ distributed throughout the steel at an inclusion density in the range 2gm/cm$^3$ to 4gm/cm$^3$. Typically the inclusions range in size between 2 and 12 microns. The cast strip has a thickness of less than 5mm and contains solidified metal oxide inclusions distributed such that the regions of the strip contain solidified inclusions to a per unit area density of at least 120 inclusions/mm$^2$.

WO 03/024644 A1

# CASTING STEEL STRIP

## TECHNICAL FIELD

This invention relates to the casting of steel strip. It has particular application to continuous casting of thin steel strip in a twin roll caster.

In twin roll casting, molten metal is introduced between a pair of contra-rotated horizontal casting rolls which are cooled so that metal shells solidify on the moving roll surfaces and are brought together at the nip between them to produce a solidified strip product delivered downwardly from the nip between the rolls. The term "nip" is used herein to refer to the general region at which the rolls are closest together. The molten metal may be poured from a ladle into a smaller vessel from which it flows through a metal delivery nozzle located above the nip so as to direct it into the nip between the rolls so forming a casting pool of molten metal supported on the casting surfaces of the rolls immediately above the nip and extending along the length of the nip. This casting pool is usually confined between side plates or dams held in sliding engagement with end surfaces of the rolls so as to dam the two ends of the casting pool against outflow, although alternative means such as electromagnetic barriers have also been proposed.

When casting thin steel strip in a twin roll caster the molten steel in the casting pool will generally be at a temperature of the order of 1500°C and above, and it is therefore necessary to achieve very high cooling rates over the casting surfaces of the rolls. It is particularly important to achieve a high heat flux and extensive nucleation on initial solidification of the steel on the casting surfaces to form the metal shells. United States Patent 5,720,336 describes how the heat flux on initial solidification can be increased by adjusting the steel melt chemistry such that a substantial proportion of the metal oxides formed as deoxidation products are liquid at the initial solidification temperature so as to form a substantially liquid layer at the interface between the molten metal and each casting surface.

As disclosed in United States Patents 5,934,359 and 6,059,014 and International Application AU 99/00641, nucleation of the steel on initial solidification can be influenced by the texture of the casting surface. In particular International Application AU 99/00641 discloses that a random texture of peaks and troughs can enhance initial solidification by providing potential nucleation sites distributed throughout the casting surfaces. We have now determined that nucleation is also dependent on the presence of oxide inclusions in the steel melt and that surprisingly it is not advantageous in twin roll strip casting to cast with "clean" steel in which the number of inclusions formed during deoxidation has been minimised in the molten steel prior to casting .

Steel for continuous casting is subjected to deoxidation treatment in the ladle prior to pouring. In twin roll casting the steel is generally subjected to silicon manganese ladle deoxidation although it is possible to use aluminum deoxidation with calcium addition to control the formation of solid $Al_2O_3$ inclusions that can clog the fine metal flow passages in the metal delivery system through which molten metal is delivered to the casting pool. It has hitherto been thought desirable to aim for optimum steel cleanliness by ladle treatment to minimise the total oxygen level in the molten steel. However we have now determined that lowering the steel oxygen level reduces the volume of inclusions and if the total oxygen content of the steel is reduced below a certain level the nature of the initial contact between the steel and roll surfaces can be adversely effected to the extent that there is insufficient nucleation to generate rapid initial solidification and high heat flux. Molten steel is trimmed by deoxidation in the ladle such that the total oxygen content falls within a range which ensures satisfactory solidification on the casting rolls and production of a satisfactory strip product. The molten steel contains a distribution of oxide inclusions (typically MnO, CaO, $SiO_2$ and/or $Al_2O_3$) sufficient to provide an adequate density of nucleation sites on the roll surfaces for initial solidification and the resulting strip product exhibits a

characteristic distribution of solidified inclusions.

## DISCLOSURE OF THE INVENTION

There is provided a method of making a steel strip by continuous casting comprising the steps of:

a. assembling a pair of cooled casting rolls having a nip between them and with confining closures adjacent the ends of the nip;

b. introducing molten low carbon steel having a total oxygen content of at least 100 ppm between the pair of casting rolls to form a casting pool between the casting rolls;

c. counter rotating the casting rolls and solidifying the molten steel to form metal shells on the surface of the casting rolls with levels of oxide inclusions reflected by the total oxygen content of the molten steel to promote the formation of thin steel strip; and

d. forming solidified thin steel strip through the nip of the casting rolls from said solidified shells.

The total oxygen content of the molten steel in the casting pool may be between 100 ppm and 250 ppm. More specifically, it may be about 200 ppm. The low carbon steel may have a carbon content in the range 0.001% to 0.1% by weight, a manganese content in the range 0.1% to 2.0% by weight and a silicon content in the range 0.01% to 10% by weight. The steel may have an aluminum content of the order of 0.01% or less by weight. The aluminum may for example be as little as 0.008% or less by weight. The molten steel may be a silicon/manganese killed steel.

The oxide inclusions are solidification inclusions and deoxidation inclusions. The solidification inclusions are formed during cooling and solidification of the steel in casting, and deoxidation inclusion are formed during deoxidation of the molten steel before casting. The solidified steel may contain oxide inclusions usually

comprised of any one or more of $MnO$, $SiO_2$ and $Al_2O_3$ distributed through the steel at an inclusion density in the range 2 $gm/cm^3$ and 4$gm/cm^3$.

The molten steel may be refined in a ladle prior to introduction between the casting rolls to form the casting pool by heating a steel charge and slag forming material in the ladle whereby to form molten steel covered by a slag containing silicon, manganese and calcium oxides. The molten steel may be stirred by injecting an inert gas into it to cause desulphurisation, and with steels such as a silicon/manganese killed steel, then injecting oxygen, to produce steel having the desired total oxygen content of at least 100 ppm and usually less than 250 ppm. The desulphurisation may reduce the sulphur content of the molten steel to less than 0.01% by weight.

The thin steel strip produced by continuous twin roll casting as described above has a thickness of less than 5 mm and is formed of a solidified steel containing solidified oxide inclusions. The distribution of the inclusions may be such that at the two the surface regions of the strip to a depth of 2 microns from the outer faces contain solidified inclusions to a per unit area density of at least 120 inclusions/$mm^2$.

The solidified steel may be a silicon/manganese killed steel and the oxide inclusions may comprise any one or more of $MnO$, $SiO_2$ and $Al_2O_3$ inclusions. The inclusions typically may range in size between 2 and 12 microns, so that at least a majority of the inclusions are in that size range.

The method described above produces a unique steel high in oxygen content distributed in oxide inclusions. Specifically, the combination of the high oxygen content in the molten steel and the short residence time of the molten steel in the casting pool results in a thin steel strip with an improved ductility properties.

## BRIEF DESCRIPTION OF THE DRAWINGS

In order that the invention may be described in more detail, some specific examples will be given with reference to

the accompanying drawings in which:

Figure 1 shows the effect of inclusion melting points on heat fluxes obtained in twin roll casting trials using silicon/manganese killed steels;

Figure 2 is an energy dispersive spectroscopy (EDS) map of Mn showing a band of fine solidification inclusions in a solidified steel strip;

Figure 3 is a plot showing the effect of varying manganese to silicon contents on the liquidus temperature of inclusions;

Figure 4 shows the relationship between alumina content (measured from the strip inclusions) and deoxidation effectiveness;

Figure 5 is a ternary phase diagram for $MnO.SiO_2.Al_2O_3$;

Figure 6 shows the relationship between alumina content inclusions and liquidus temperature;

Figure 7 shows the effect of oxygen in a molten steel on surface tension; and

Figure 8 is a plot of the results of calculations concerning the inclusions available for nucleation at differing steel cleanliness levels.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

We have conducted extensive casting trials on a twin roll caster of the kind fully described in United States Patents 5,184,668 and 5,277,243 to produce steel strip of the order of 1 mm thick and less. Such casting trials using silicon manganese killed steel have demonstrated that the melting point of oxide inclusions in the molten steel have an effect on the heat fluxes obtained during steel solidification as illustrated in Figure 1. Low melting point oxides improve the heat transfer contact between the molten metal and the casting roll surfaces in the upper regions of the pool, generating higher heat transfer rates. Liquid inclusions are not produced when the melting point is greater than the steel temperature in the casting pool. Therefore, there is a dramatic reduction in heat transfer rate when the inclusion

melting point is greater than approximately 1600°C.

Casting trials with aluminum killed steels have shown that in order to avoid the formation of high melting point alumina inclusions (melting point 2050°C) it is necessary to have calcium treatment to provide liquid $CaO.Al_2O_3$ inclusions.

The oxide inclusions formed in the solidified metal shells and in turn the thin steel strip comprise inclusions formed during cooling and solidification of the steel, and deoxidation inclusions formed during refining in the ladle.

The free oxygen level in the steel is reduced dramatically during cooling at the meniscus, resulting in the generation of solidification inclusions near the surface of the strip. These solidification inclusions are formed predominantly of $MnO.SiO_2$ by the following reaction:

$$Mn+Si+3O = MnO.SiO_2$$

The appearance of the solidification inclusions on the strip surface, obtained from an Energy Dispersive Spectroscopy (EDS) map, is shown in Figure 2. It can be seen that solidification inclusions are extremely fine (typically less than 2 to 3μm) and are located in a band located within 10 to 20μm from the surface. A typical size distribution of the inclusions through the strip is shown in Figure 3 of our paper entitled Recent Developments in Project M the Joint Development of Low Carbon Steel Strip Casting by BHP and IHI, presented at the METEC Congress 99, Dusseldorf Germany (June 13-15, 1999)

The comparative levels of the solidification inclusions is primarily determined by the Mn and Si levels in the steel. Figure 3 shows that the ratio of Mn to Si has a significant effect on the liquidus temperature of the inclusions. A manganese silicon killed steel having a carbon content in the range of 0.001% to 0.1% by weight, a manganese content in the range 0.1% to 2.0% by weight and a silicon content in the range 0.1% to 10% by weight and an aluminum content of the order of 0.01% or less by weight can produce

such oxide inclusions during cooling of the steel in the upper regions of the casting pool. In particular the steel may have the following composition, termed M06:

| | |
|---|---|
| Carbon | 0.06% by weight |
| Manganese | 0.6% by weight |
| Silicon | 0.28% by weight |
| Aluminium | 0.002% by weight. |

Deoxidation inclusions are generated during deoxidation of the molten steel in the ladle with Al, Si and Mn. Thus, the composition of the oxide inclusions formed during deoxidation is mainly $MnO.SiO_2.Al_2O_3$ based. These deoxidation inclusions are randomly located in the strip and are coarser than the solidification inclusions near the strip surface.

The alumina content of the inclusions has a strong effect on the free oxygen level in the steel. Figure 4 shows that with increasing alumina content, free oxygen in the steel is reduced. With the introduction of alumina, $MnO.SiO_2$ inclusions are diluted with a subsequent reduction in their activity, which in turn reduces the free oxygen level, as seen from the reaction below:

$$Mn + Si + 3O + Al_2O_3 \Leftrightarrow (Al_2O_3).MnO.SiO_2.$$

For $MnO-SiO_2-Al_2O_3$ based inclusions, the effect of inclusion composition on liquidus temperature can be obtained from the ternary phase diagram shown in Figure 5. Analysis of the oxide inclusions in the thin steel strip has shown that the $MnO/SiO_2$ ratio is typically within 0.6 to 0.8 and for this regime, it was found that alumina content of the oxide inclusions had the strongest effect on the inclusion melting point (liquidus temperature), as shown in Figure 6.

We have determined that it is important for casting in accordance with the present invention to have the solidification and deoxidation inclusions such that they are liquid at the initial solidification temperature of the steel

and that the molten steel in the casting pool have an oxygen content of at least 100 ppm to produce metal shells with levels of oxide inclusions reflected by the total oxygen content of the molten steel to promote nucleation and high heat flux during the initial solidification of the steel on the casting roll surfaces. Both solidification and deoxidation inclusions are oxide inclusions and provide nucleation sites and contribute significantly to nucleation during the metal solidification process, but the deoxidation inclusions are ultimately rate controlling in that their concentration can be varied. The deoxidation inclusions are much bigger, typically greater than 4 microns, whereas the solidification inclusions are generally less than 2 microns and are MnO. $SiO_2$ based and have no $Al_2O_3$ whereas the deoxidation inclusions also have $Al_2O_3$

It has been found in casting trials using the above M06 grade of silicon/manganese killed steel that if the total oxygen content of the steel is reduced in the ladle refining process to low levels of less than 100 ppm, heat fluxes are reduced and casting is impaired whereas good casting results can be achieved if the total oxygen content is at least above 100 ppm and typically on the order of 200 ppm. The total oxygen content may be measured by a "Leco" instrument and is controlled by the degree of "rinsing" during ladle treatment, i.e. the amount of argon bubbled through the ladle via a porous plug or top lance, and the duration of the treatment. The total oxygen content was measured by conventional procedures using the LECO TC-436 Nitrogen/Oxygen Determinator described in the TC 436 Nitrogen/Oxygen Determinator Instructional Manual available from LECO (Form No. 200-403, Rev. Apr. 96, Section 7 at pp. 7-1 to 7-4.

In order to determine whether the enhanced heat fluxes obtained with higher total oxygen contents was due to the availability of oxide inclusions as nucleation sites, casting trials were carried out with steels in which deoxidation in the ladle was carried out with calcium silicide (Ca-Si) and the results compared with casting with the low carbon Si-killed steel known as M06 grades of steel. The results are set out in the following table:

Table 1

Heat flux differences between M06 and Cal-Sil grades.

| Cast No. | Grade | Casting speed, (m/min) | Pool Height, (mm) | Total heat Removed (MW) |
|---|---|---|---|---|
| M 33 | M06 | 64 | 171 | 3.55 |
| M 34 | M06 | 62 | 169 | 3.58 |
| O 50 | Cal-Sil | 60 | 176 | 2.54 |
| O 51 | Cal-Sil | 66 | 175 | 2.56 |

Although Mn and Si levels were similar to normal Si-killed grades, the free oxygen level in Ca-Si heats was lower and the oxide inclusions contained more CaO. Heat fluxes in Ca-Si heats were lower despite a lower inclusion melting point (See Table 2).

Table 2

Slag compositions with Ca-Si deoxidation

| Grade | Free Oxygen (ppm) | Slag Composition (wt %) | | | | Inclusion melting temperature (°C) |
|---|---|---|---|---|---|---|
| | | $SiO_2$ | MnO | $Al_2O_3$ | CaO | |
| Ca-Si | 23 | 32.5 | 9.8 | 32.1 | 22.1 | 1399 |

Oxygen levels in Ca-Si grades were lower, typically 20 to 30 ppm compared to 40 to 50 ppm with M06 grades. Oxygen is a surface active element and thus reduction in oxygen level is expected to reduce the wetting between molten steel and the casting rolls and cause a reduction in the heat transfer rate. However, from Figure 7 it appears that oxygen reduction from 40 to 20 ppm may not be sufficient to increase the surface tension to levels that explain the observed reduction in the heat flux.

It can be concluded that lowering the oxygen level

in the steel reduces the volume of inclusions and thus reduces the number of oxide inclusions for initial nucleation. This has the potential to adversely impact the nature of the initial contact between steel and the roll surface. Dip testing work has shown that a nucleation per unit area density of about 120/mm$^2$ is required to generate sufficient heat flux on initial solidification in the upper or meniscus region of the casting pool. Dip testing involves advancing a chilled block into a bath of molten steel at such a speed as to closely simulate the conditions at the casting surfaces of a twin roll caster. Steel solidifies onto the chilled block as it moves through the molten bath to produce a layer of solidified steel on the surface of the block. The thickness of this layer can be measured at points throughout its area to map variations in the solidification rate and therefore the effective rate of heat transfer at the various locations. It is thus possible to produce an overall solidification rate as well as total heat flux measurements. It is also possible to examine the microstructure of the strip surface to correlate changes in the solidification microstructure with the changes in observed solidification rates and heat transfer values and to examine the structures associated with nucleation on initial solidification at the chilled surface. A dip testing apparatus is more fully described in United States Patent 5,720,336

The relationship of the oxygen content of the liquid steel on initial nucleation and heat transfer has been examined using a model described in Appendix 1. This model assumes that all the oxide inclusions are spherical and are uniformly distributed throughout the steel. A surface layer was assumed to be 2 μm and that only inclusions present in that surface layer could participate in the nucleation process on initial solidification of the steel. The input to the model was total oxygen content in the steel, inclusion diameter, strip thickness, casting speed, and surface layer thickness. The output was the percentage of inclusions of the total in the steel required to meet a targeted nucleation per unit area density of 120/mm$^2$.

Figure 8 is a plot of the percentage of oxide inclusions in the surface layer required to participate in the nucleation process to achieve the target nucleation per unit area density at different steel cleanliness levels as expressed by total oxygen content, assuming a strip thickness of 1.6 mm and a casting speed of 80/min. This shows that for a 2 μm inclusion size and 200 ppm total oxygen content, 20% of the total available oxide inclusions in the surface layer are required to achieve the target nucleation per unit area density of 120/mm$^2$. However, at 80 ppm total oxygen content, around 50% of the inclusions are required to achieve the critical nucleation rate and at 40 ppm total oxygen level there will be an insufficient level of oxide inclusions to meet the target nucleation per unit area density. Accordingly when trimming the steel by deoxidation in the ladle, the oxygen content of the steel can be controlled to produce a total oxygen content in the range 100 to 250 ppm and typically about 200 ppm. This will have the result that the two micron deep layers adjacent the casting rolls on initial solidification will contain oxide inclusions having a per unit area density of at least 120/mm$^2$. These inclusions will be present in the outer surface layers of the final solidified strip product and can be detected by appropriate examination, for example by energy dispersive spectroscopy (EDS).

**EXAMPLE**

INPUTS

| | | |
|---|---|---|
| Critical nucleation per unit area density no/mm2 (needed to achieve sufficient heat transfer rates) testing work | 120 | This value has been obtained from experimental dip |
| Roll width m | 1 | |
| Strip thickness mm | 1.6 | |
| Ladle tonnes t | 120 | |
| Steel density, kg/m3 | 7800 | |
| Total oxygen, ppm | 75 | |
| Inclusion density, kg/m3 | 3000 | |

OUTPUTS

| | | |
|---|---|---|
| Mass of inclusions, kg | 21.42857 | |
| Inclusion diameter, m | 2.00E-06 | |
| Inclusion volume, m3 | 0.0 | |
| Total no of inclusions | 1706096451319381.5 | |
| Thickness of surface layer, um (one side) | 2 | |
| Total no of inclusions surface only nucleation process | 4265241128298.4536 | These inclusions can participate in the initial |

| | |
|---|---|
| Casting speed, m/min | 80 |
| Strip length, m | 9615.38462 |
| Strip surface area, m2 | 19230.76923 |
| Total no of nucleating sites required | 2307692.30760 |
| % of available inclusions that need to participate in the nucleation process | 54.10462 |

APPENDIX 1

List of symbols

$w$ = roll width, m

$t$ = strip thickness, mm

$m_s$ = steel weight in the ladle, tonne

$\rho_s$ = density of steel, kg/m$^3$

$\rho_i$ = density of inclusions, kg/m3

$O_t$ = total oxygen in steel, ppm

$d$ = inclusion diameter, m

$v_i$ = volume of one inclusions, m3

$m_i$ = mass of inclusions, kg

$N_t$ = total number of inclusions

$t_s$ = thickness of the surface layer, um

$N_s$ = total number of inclusions present in the surface (that can participate in the nucleation process)

$u$ = casting speed, m/min

$L_s$ = strip length, m

$A_s$ = strip surface area, m2

$N_{req}$= Total number of inclusions required to meet the target nucleation density

$NC_t$ = target nucleation per unit area density, number/mm2 (obtained from dip testing)

$N_{av}$ = % of total inclusions available in the molten steel at the surface of the casting rolls for initial nucleation process.

Equations

$m_i$= ($O_t$ x $m_s$ x 0.001)/0.42

Note: for Mn-Si killed steel, 0.42kg of oxygen is needed to produce 1 kg of neclusions with a composition of 30% MnO, 40% $SiO_2$ and 30% $Al_2O_3$.

For Al-killed steel (with Ca injection), 0.38 kg of

oxygen is required to produce 1 kg of inclusions with a composition of 50% $Al_2O_3$ and 50% CaO.

$v_i = 4.19 \times (d/2)^3$

(3) $N_t = m_i / (\rho_i \times v_i)$

(4) $N_s = (2.0\ t_s \times 0.001 \times N_t/t)$

(5) $L_s = (m_s \times 1000)/(\rho_s \times w \times t/1000)$

(6) $A_s = 2.0 \times L_s \times w$

$N_{req} = A_s \times 10^6 \times NC_t$

(8) $N_{av}\ \% = (N_{req}/N_s) \times 100.0$

Eq. 1 calculates the mass of inclusions in steel.

Eq. 2 calculates the volume of one inclusion assuming they are spherical.

Eq. 3 calculates the total number of inclusions available in steel.

Eq. 4 calculates the total number of inclusions available in the surface layer (assumed to be 2 um on each side). Note that these inclusions can only participate in the initial nucleation.

Eq. 5 and Eq. 6 used to calculate the total surface area of the strip.

Eq. 7 calculates the number of inclusions needed at the surface to meet the target nucleation rate.

Eq. 8 is used to calculate the percentage of total inclusions available at the surface which must participate in the

nucleation process. Note if this number is great than 100%, then the number of inclusions at the surface is not sufficient to meet target nucleation rate.

CLAIMS:

1. A method of making a steel strip by continuous casting comprising the steps of:

a. assembling a pair of cooled casting rolls having a nip between them and with confining closures adjacent the ends of the nip;
b. introducing molten low carbon steel having a total oxygen content of at least 100 ppm between the pair of casting rolls to form a casting pool between the casting rolls;
c. counter rotating the casting rolls and solidifying the molten steel to form metal shells on the surface of the casting rolls with levels of oxide inclusions reflected by the total oxygen content of the molten steel to promote the formation of thin steel strip; and
d. forming solidified thin steel strip through the nip of the casting rolls from said solidified shells.

2. A method of making steel strip as claimed in Claim 1, wherein the molten steel in the casting pool has carbon content in the range of 0.001% to 0.01% by weight, a manganese content in the range of 0.01% to 2.0% by weight, and a silicon content in the range of 0.01% to 10% by weight.

3. A method of making steel strip as claimed in Claim 2 wherein the molten steel in the casting pool has an aluminum content on the order of 0.01% or less by weight.

4. A method of making steel strip as claimed any one of the preceding claims, wherein the molten steel in the casting pool has an oxygen content between 100 ppm and 250 ppm.

5. A method of making steel strip as claimed in any one of the preceding claims, wherein the molten steel contains oxide inclusions comprising any one or more of $MnO$, $SiO_2$ and $Al_2O_3$ distributed through the steel at an inclusion density in the range 2 $gm/cm^3$ to 4 $gm/cm^3$.

6. A method of making steel strip as claimed in any one of the preceding claims, wherein more than a majority of the inclusions range in size between 2 and 12 microns.

7. A method of making steel strip as claimed in any one of the preceding claims, wherein the sulphur content of the molten steel is less than 0.01% by weight.

8. A method of making steel strip as claimed in Claim 1, comprising the additional steps of:

e. refining the molten steel in the ladle prior to forming the casting pool by heating a steel charge and slag forming material in the ladle to form molten steel covered by a slag containing silicon, manganese and calcium oxides, stirring the molten steel in the ladle by injecting an inert gas into molten steel to cause desulphurisation, and thereafter injecting oxygen to produce molten steel having the total oxygen content of greater than 100ppm.

9. A method of making steel strip as claimed in Claim 8, wherein the desulphurisation reduces the sulphur content of the molten steel to less than 0.01% by weight.

10. A method of making a thin steel strip as claimed in Claim 8 or 9, wherein the solidified steel is a silicon/manganese killed steel and the inclusions comprise any one or more of $MnO$, $SiO_2$ and $Al_2O_3$.

11. A method of making a thin steel strip as claimed in any one of Claims 8 to 10, wherein more than a majority of the inclusions range in size between 2 and 12 microns.

12. A method of making a steel strip as claimed in any one of Claims 8 to 11, wherein the solidified steel has a total oxygen content in the range of 100 ppm to 250 ppm.

13. A thin steel strip produced by twin roll casting to a thickness of less than 5mm and formed of a solidified steel containing solidified oxide inclusions distributed such that at surface regions of the strip to a depth of 2 microns from

the surface contain such inclusions to a per unit area density of at least 120 inclusions/$mm^2$.

14. A thin steel strip as claimed in Claim 13, wherein the majority of the solidified steel is a silicon/manganese killed steel and the inclusions comprise any one or more of $MnO$, $SiO_2$ and $Al_2O_3$.

15. A thin steel strip as claimed in Claim 13 or Claim 14, wherein the majority of the inclusions range in size between 2 and 12 microns.

16. A thin steel strip as claimed in any one of Claims 13 to 15, wherein the solidified steel has a total oxygen content in the range 100 ppm to 250 ppm.

17. A thin steel strip produced by twin roll casting to a thickness of less than 5 mm and formed of a solidified steel containing oxide inclusions distributed to reflect an oxygen content in the solidified steel in the range 100 ppm to 250 ppm.

18. A thin steel strip as claimed in Claim 17, wherein the majority of the solidified steel is a silicon/manganese killed steel and the inclusions comprise any one or more of $MnO$, $SiO_2$ and $Al_2O_3$.

19. A thin steel strip as claimed in Claim 17 or Claim 18, wherein the majority of the inclusions range in size between 2 and 12 microns.

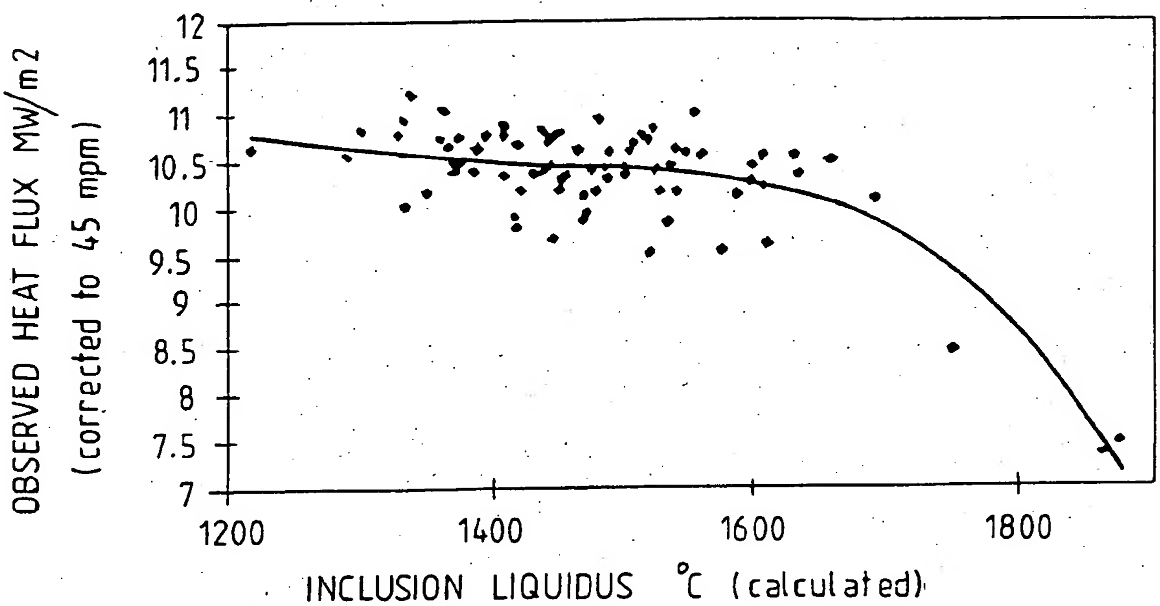

OBSERVED HEAT FLUX MW/m2
(corrected to 45 mpm)
12
11.5
11
10.5
10
9.5
9
8.5
8
7.5
7
1200
1400
1600
1800
INCLUSION LIQUIDUS °C (calculated)

FIG. 1.

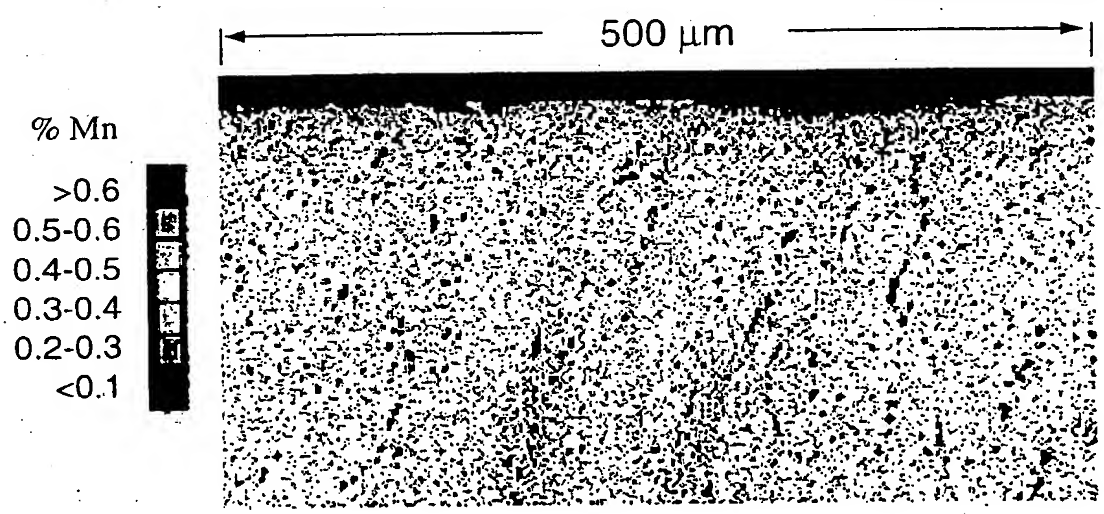

500 μm
% Mn
>0.6
0.5-0.6
0.4-0.5
0.3-0.4
0.2-0.3
<0.1

FIG. 2.

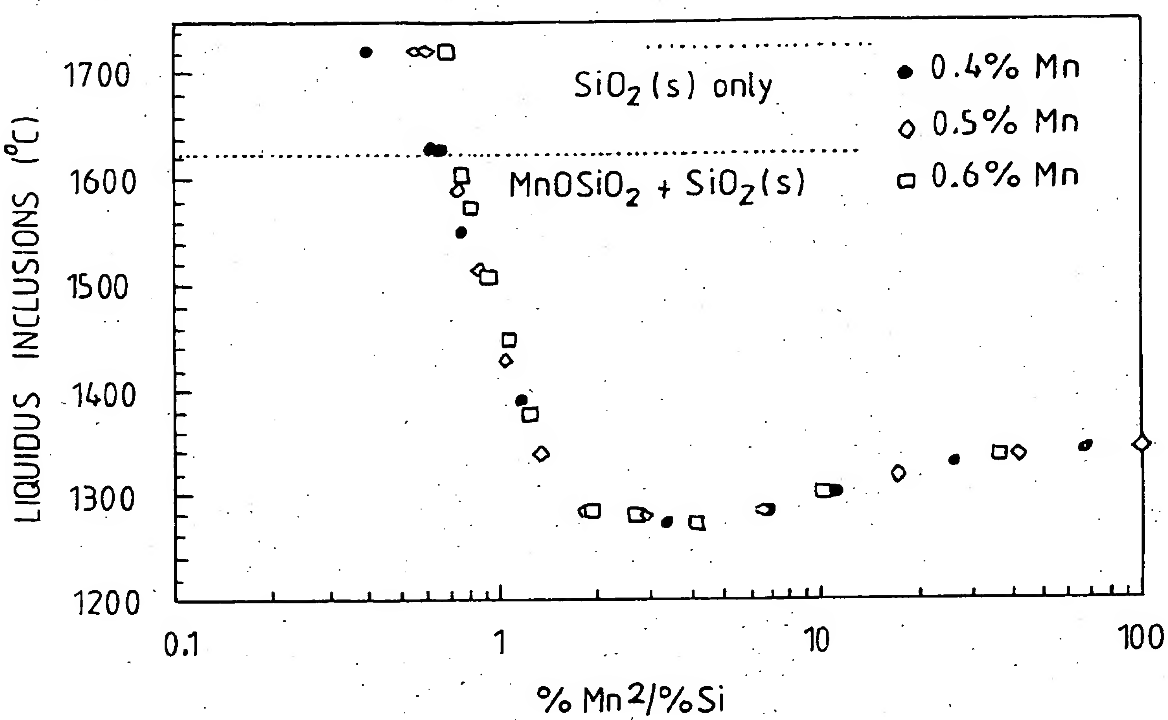

1700
1600
1500
1400
1300
1200
LIQUIDUS INCLUSIONS (°C)
SiO2 (s) only
MnOSiO2 + SiO2(s)
0.4% Mn
0.5% Mn
0.6% Mn
0.1
1
10
100
% Mn2/%Si

FIG. 3.

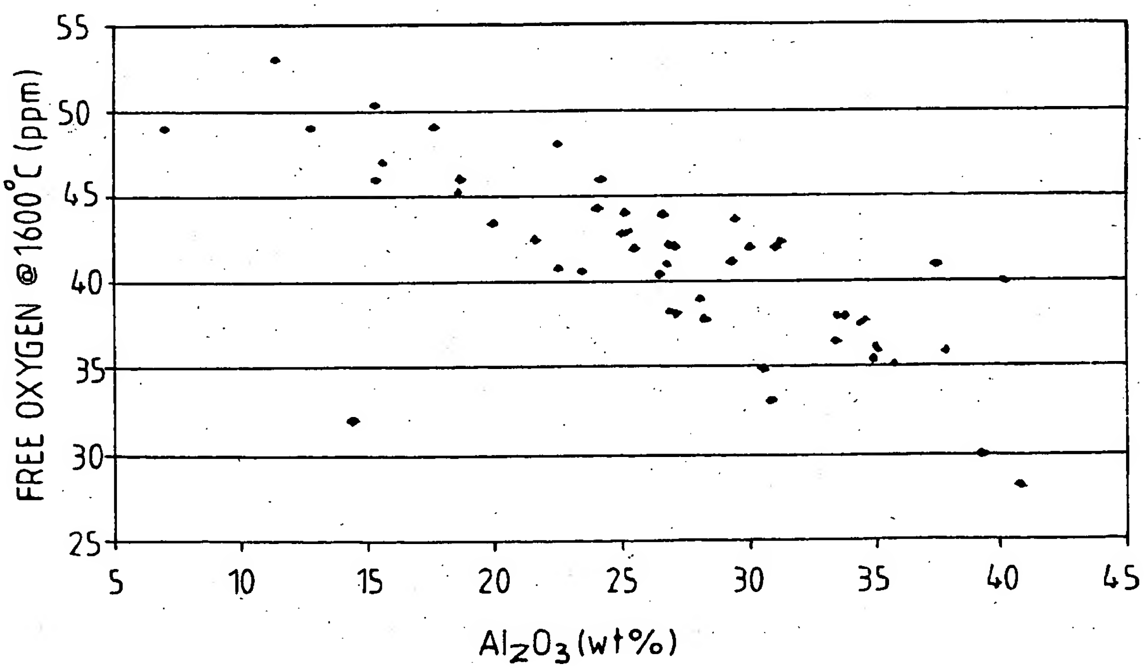
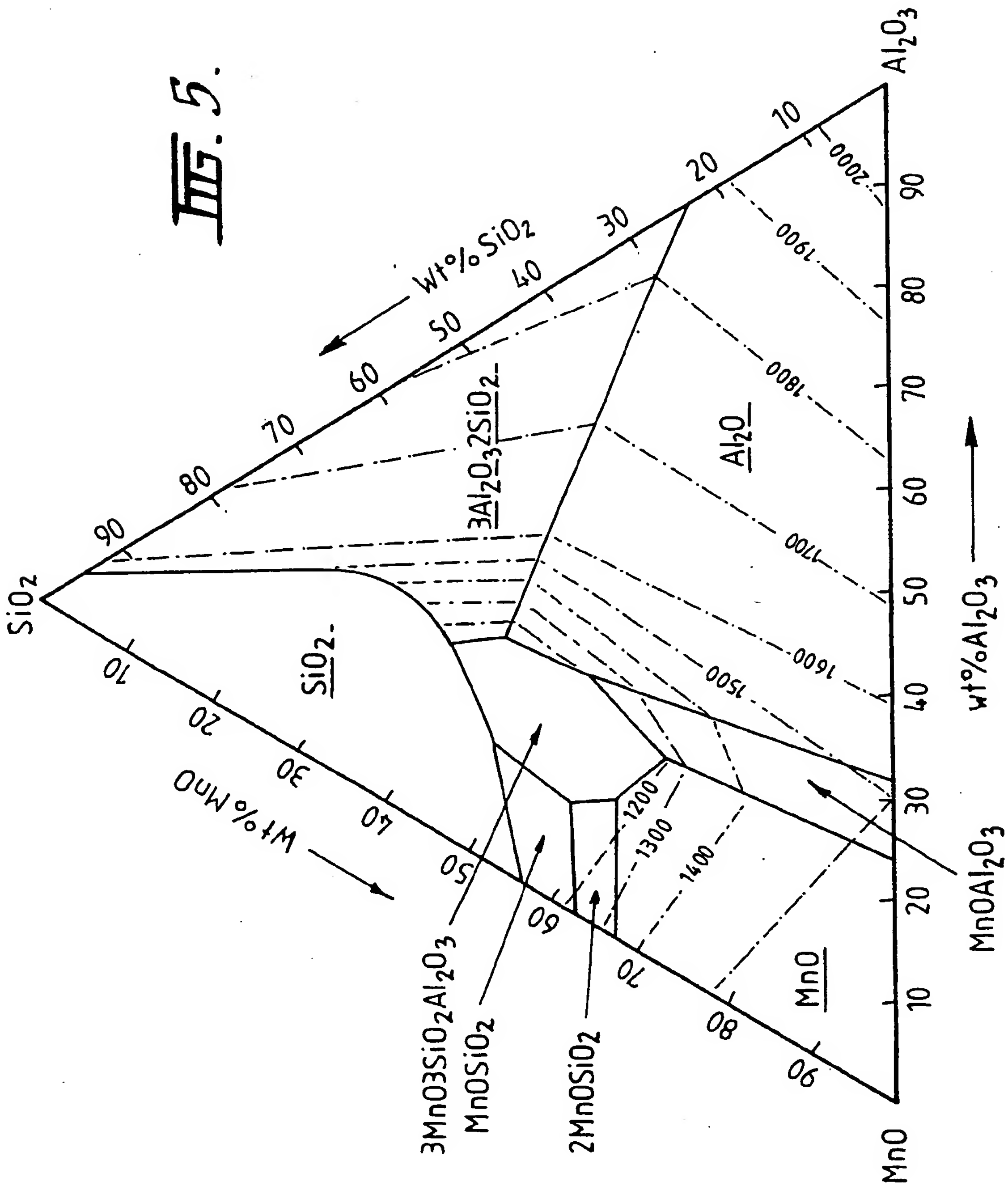
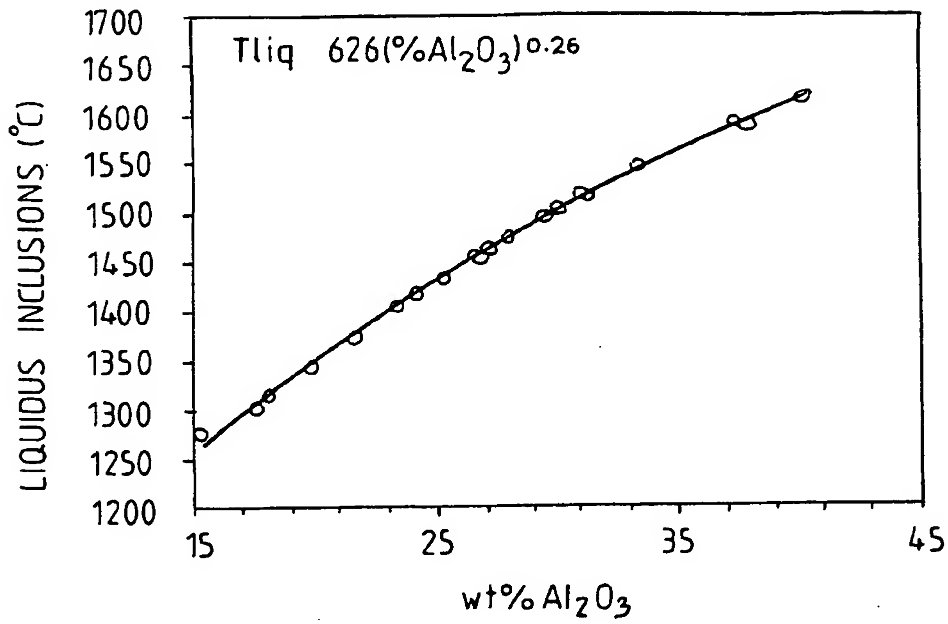

55
50
45
40
35
30
25
FREE OXYGEN @1600°C (ppm)
5
10
15
20
25
30
35
40
45
Al2O3 (wt%)

FIG. 4.

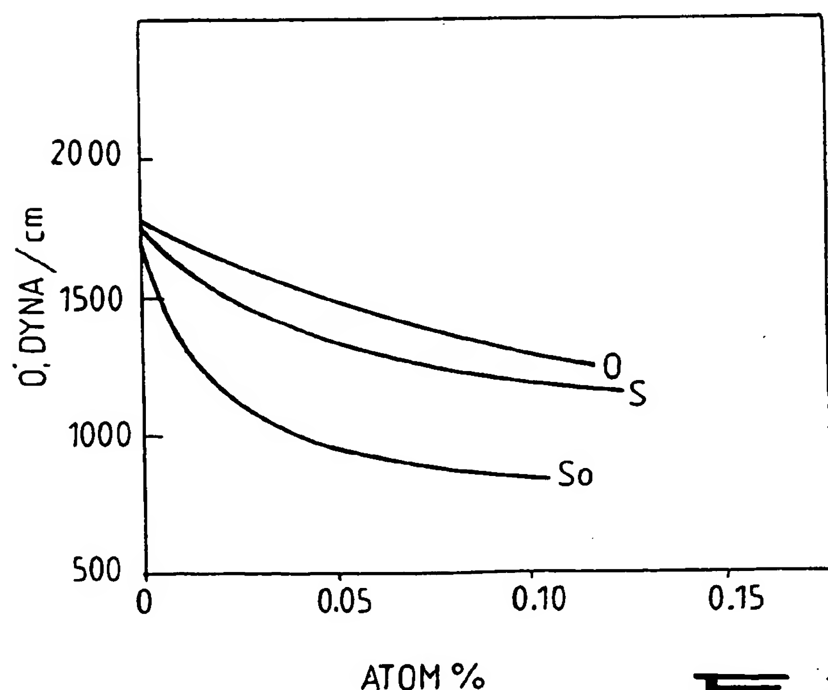
FIG. 5.


SiO2
Al2O3
MnO
Wt% SiO2
Wt% MnO
wt% Al2O3
SiO2
Al2O
MnO
3Al2O3 2SiO2
MnOAl2O3
3MnO3SiO2Al2O3
MnOSiO2
2MnOSiO2
2000
1900
1800
1700
1600
1500
1400
1300
1200



Tliq 626(%Al2O3)0.26
LIQUIDUS INCLUSIONS (°C)
1700
1650
1600
1550
1500
1450
1400
1350
1300
1250
1200
15
25
35
45
wt% Al2O3


FIG. 6.



σ, DYNA/cm
2000
1500
1000
500
0
0.05
0.10
0.15
ATOM %
O
S
So


FIG. 7.

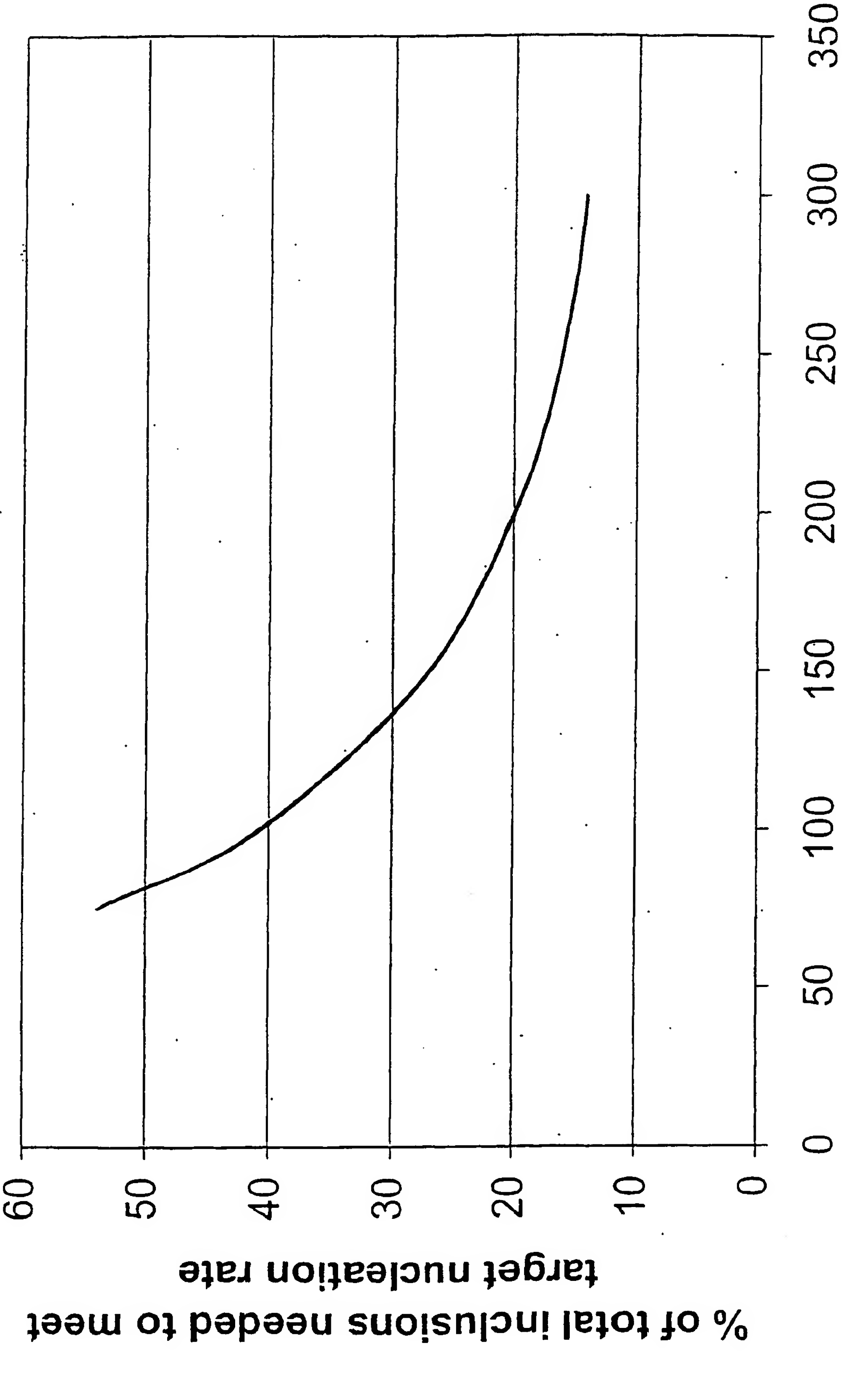

% of total inclusions needed to meet target nucleation rate
0
10
20
30
40
50
60
Total oxygen (ppm)
0
50
100
150
200
250
300
350

FIG. 8.

# INTERNATIONAL SEARCH REPORT

International application No.
**PCT/AU02/01257**

**A. CLASSIFICATION OF SUBJECT MATTER**

Int. Cl. 7: B22D 11/06

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
REFER TO ELECTRONIC DATA BASE CONSULTED

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DWPI, IPC: B22D 11/06, OXIDE+, OXYGEN

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 5934359 A (STREZOV) 10 August 1999<br>Col 2, lines 39 to 58, col 6, line 63 to col 7, line 5 and claims 11, 14 | 1, 4, 7, 17, 18 |
| X | US 6059014 A (STREZOV) 9 May 2000<br>Col 2, lines 50 to 64, col 6, line 55 to col 7, line12 and claim 14 | 1, 4, 7, 17, 18 |
| X | Patent abstracts of Japan, JP 02-205618 A (NIPPON STEEL CORP) 15 August 1990<br>Whole abstract | 1, 4, 7, 17 |

[X] Further documents are listed in the continuation of Box C  [X] See patent family annex

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search
18 October 2002

Date of mailing of the international search report
29 OCT 2002

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## INTERNATIONAL SEARCH REPORT

International application No.
**PCT/AU02/01257**

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|---|---|---|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X | Patent Abstracts of Japan, JP 03-291139 A (NIPPON STEEL CORP) 20 December 1991<br>Whole abstract | 1-4, 7, 17, 18 |
| A,P | WO 02/26422 A (ISHIKAWAJIMA-HARIMA HEAVY INDUSTRIES COMPANY LTD) 4 April 2002<br>Whole document | 1-19 |

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
**PCT/AU02/01257**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent Document Cited in Search Report | | Patent Family Member | | | | | |
|---|---|---|---|---|---|---|---|
| US | 5934359 | AU | 17830/97 | BR | 9701849 | CA | 2202240 |
| | | CN | 1170647 | EP | 800881 | JP | 10029047 |
| | | NZ | 314421 | ZA | 9702595 | | |
| US | 6059014 | US | 5934359 | AU | 17830/97 | BR | 9701849 |
| | | CA | 2202240 | CN | 1170647 | EP | 800881 |
| | | JP | 10029047 | NZ | 314421 | ZA | 9702595 |
| JP | 2205618 | NONE | | | | | |
| JP | 3291139 | NONE | | | | | |
| WO | 200226422 | AU | 20000479 | AU | 200191499 | US | 2002043357 |

END OF ANNEX